KEROGEN-RICH MICROMETEORITES AND CRUDE PETROLEUM IN HADEAN TIME. M.Maurette[1], A. Brack[2], J.Duprat[1], C.Engrand[1] [1]CSNSM, 91405 Orsay Campus, France, maurette@csnsm.in2p3.fr; [2]CBM, Rue Charles Sadron, 45071 Orleans Cedex 2, France.

Delivery of micrometeorite kerogen to the Hadean oceanic crust. Kerogens are abundant by-products of incomplete combustion, pyrolysis and radiation reprocessing of almost any kinds of organic precursors. Therefore they are observed in a wide variety of environments, including: – terrestrial shales, – the fine-grained matrix of hydrous-carbonaceous chondrites (HCCs) such as Murchison; – the interstellar medium; – the exhaust pipes of cars. In the absence of microorganisms that can digest it, kerogen is one of the most durable and insoluble classes of organic compounds known. In particular it resists to both strong acids and ordinary organic solvents. The acid resistant residue of Murchison is essentially made of kerogen with an approximate formula, $C_{100}H_{48}N_{1.8}S_2 0_{12}$ [1]. On Earth, important substances are derived from some parent kerogen. They include petroleum and varieties of activated carbon.

The ion microprobe analysis of 28 Antarctic micrometeorites (AMMs) yielded their average C content of about 2.5 wt.% (see Fig. 5, in Ref. 2). The nuclear microprobe measurements of the C and N contents of AMMs and HCCs [3] indicated that their major carbonaceous components are rather similar, being composed of kerogen with a C/N ratio varying from ~25 to ~50. This is also compatible with previous studies including: **(i)** analyses of much larger aliquot of HCCs by GCMS [1]; **(ii)** microanalyses of AMMs and CM-, CI- and CV-types carbonaceous chondrites with a double laser desorption-ionization mass spectrometer that revealed the mass spectra of the building blocks of their constituent kerogen, which are polycyclic aromatic hydrocarbons (i.e., PAH-moieties) [4]; **(iii)** microanalyses of AMMs with a Fourier Transform IR microscope [5].

In our EMMA scenario (Early micrometeorite Accretion) a huge mass influx of juvenile micrometeorites delivered about 5×10^{24} g of micrometeorites during the first ~200 Ma of the post-lunar period of the *Late Heavy Bombardment* (*LHBomb*) [2, 6] –i.e., a value twice as high as the total mass of the current asteroidal belt. The study of our new collection of unweathered micrometeorites collected in surface snow from Central Antarctica shows that about 20 wt.% of the incoming micrometeorites survive unmelted upon atmospheric entry.

A large fraction of them was deposited on the early oceanic crust, which was formed very soon after the formation of the Moon, about 4.4 Ga ago [7]. Assuming that about 50% of the early Earth's surface was covered with oceans, the total amount of kerogen deposited in the deep sea (sediments) (~1.6×10^{22}g) was equivalent to a ~30 m thick global layer, whereas the value estimated for organics trapped in the present day biosphere is about 10 cm. What was the fate of this kerogen? Could it have been involved in the prebiotic chemistry of life even though it is considered as one of the most inert organics?

Kerogen-rich shales on Earth (all the information about petroleum used in this abstract have been extracted from the *Wikipedia Encyclopedia* and from searches on Google). On the Earth, bitumen- and kerogen-rich shales are the source rocks of fossil fuels including crude petroleum.

There are two conflicting models about the formation of petroleum. In the biogenic scenario most crude petroleum exploited today is derived from tiny plants and organisms that thrive in the top layers of the oceans (i.e., plankton). When they die they accumulate on the sea floor (like unmelted micrometeorites carrying kerogen), where they are trapped in sediments that get steadily buried. At depths larger than a few hundreds meters, their residual organics yield kerogen whereas sea sediments are transformed into shales. Then at larger depths (up to about 6 km) the heat and pressure break down the kerogen to form crude petroleum (by "catagenesis") that migrates upward and can be trapped in porous rocks thus forming petroleum reserves. Those exploited today were mostly formed in the Jurassic oceans.

However, the so-called Russian-Ukrainian "oil-connection" has challenged the biogenic origin of petroleum since the 1860's! These scientists argue that petroleum would have been formed at the high pressures and temperatures produced at depths ≥200 km in the upper mantle. In their model, the source material was just inherited from the building material of the Earth. Then at some point petroleum leaked upward, etc. Western geologists have now reluctantly accepted the view that abiogenic petroleum exists. However, it could not have been produced in significant quantities compared to the biogenic variety exploited today.

Fate of the kerogen-rich micrometeorites on the oceanic crust. Two simple similarities were noted between terrestrial and micrometeoritic kerogens: **(i)** Kerogen-rich shales originate from the initial mixture of clays, mud and silts that get deposited on the floors of sedimentary basins and oceans. About 50% of the mass of AMMs is made of a fine grained matrix of clays in which kind of silt particles are embedded. These minerals will be partially metamorphosed into

shale-like grains, which will become encrusted in the normal terrestrial shale formed at about the same depths; **(ii)** Terrestrial shales are called as kerogen-rich rocks when they contain about 2 wt% of kerogen. Surprisingly, this threshold value corresponds to the average content of kerogen in AMMs.

Consequently, kerogen-rich micrometeorites would have followed an abiogenic fate that surprisingly well mimics the biogenic fate of dead plankton. The story outlined in the previous section for dead plankton, directly applies to micrometeorites and their major component of kerogen: *they accumulate on the sea floor where they are trapped in sediments that get steadily buried. At depths larger than a few hundreds meters …. the heat and pressure break down kerogen to form crude petroleum that migrates upward … thus forming petroleum reserves*.

A gigantic "black tide" in prebiotic chemistry? There was however a major difference between Jurassic times and the *LHBomb* area, prior to ~4 Ga ago, when the micrometeoric mass influx and the impact rates of ≥1 km size bodies were much enhanced. Impact fracturing unavoidably led to some giant spills of the abiogenic petroleum that would have ended up floating "for ever" on the surface of the oceans.

The stage was ready for the plausible formation of a gigantic ***black tide*** that spread over most of the Earth's surface. As petroleum is one of the richest sources of organics this black tide would have dominantly fed any prebiotic soup – the concept of a "soup" was first proposed by Oparin about 100 years ago, in which the starting materials were metallic carbides and nitrides that interacted with O_2 and H_2O in the early atmosphere. Furthermore, the degradation products of micrometeoric kerogen upon frictional heating further enriched the prebiotic soup [6].

Reprocessing of micrometeoritic kerogen upon atmospheric entry. Micrometeorites that are destroyed along their deceleration range in the thermosphere, either by volatilization or melting (i.e., about 80% of the incoming flux) generate a kind of complex cosmic smoke. It should carry a mixture of very small (≤100 nm) particles, gases and ions, which is very poorly characterized yet. It probably included: – major greenhouse gases such as SO_2, H_2O and CO_2 (they are mostly generated by the iron sulfides, hydrous minerals and the carbonates and carbonaceous components of micrometeorites, respectively); – hydrogenated carbon particles; – char particles; – PAHs-moieties; – nuggets of ferrihydrite; – metallic oxides; – metallic ions, such as iron, which is the dominating ion in the E-layer of the thermosphere.

This high elevation smoke gravitationally settled down throughout the lower atmospheric layers. This unique capability of micrometeoritic "volcanism" to distribute homogeneously the smoke from the "top", all over the Earth's surface might have drastically accelerated prebiotic chemistry. A fraction of the degassed water was photodissociated, thus generating H_2. The smoke particles would be exposed during their slow descent in the atmosphere to other reactive species such as SO_2, NO_x, O_3. In particular, after thermalization, most of these species would react with the hydrogenated carbon particles and the PAHs-moieties released by micrometeorites. This is expected to produce nitro-PAHs, ketones and quinines [8, 9], as well as other kinds of odd petroleum distillates [6]. Moreover, the variety of nanophase smoke particles likely opened a new kind of efficient *organo-mineral chemistry* of life.

Oddly enough, the initial inert kerogen of extraterrestrial matter, which has been disregarded for so long as a reactant in prebiotic chemistry, would have been converted back into much more reactive substances. Even though we cannot assess as yet the efficiency of transformation of micrometeoritic kerogen into petroleum, this first essay in *kerogenetics* supports the previous conclusion that micrometeorites opened a large variety of reaction channels in the prebiotic chemistry of life [6]. Unavoidably, they would have played a major role in the birth of life on the Earth, and possibly on Mars and many planets orbiting other Suns imbedded in a dusty debris disk [10].

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